p-tert-Butylcalix[4]arene Derivatives Containing Azathiol Receptors and Their Recognition towards Hg(II)

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Abstract. 25,27(2,2′-bis(ethoxybenzyl))-1,9-diimine-3,7-dithianonane-*p-tert*-butylcalix[4]arene (**3**), 25,27(4,4′-bis(ethoxybenzyl))-1,9-diimine-3,7-dithianonane-*p-tert*-butylcalix[4]arene (**4**), 25,27(2,2′-bis(ethoxybenzyl))-1,8-diimine-3,6-dithianonane-*p-tert*-butylcalix[4]arene (**5**) and 25,27(4,4′-bis(ethoxybenzyl))-1,8-diimine-3,6-dithianonane-*p-tert*-butylcalix[4]arene (**6**) have been synthesized by condensation reactions between 25,27(2,2′-bis(ethoxybenzaldehyde))-*p-tert*-butylcalix[4]arene (**1**) and 25,27(4,4′-bis(ethoxybenzaldehyde))-*p-tert*-butylcalix[4]arene (**2**) and appropriate amines. Reduction of **3** and **4** with $NaBH_4$ and subsequent protonation by HCl/CH_3OH resulted in 25,27(2,2′-bis(ethoxybenzyl))-1,9-diaza-3,7-dithianonane-*p-tert*-butylcalix[4]arene dihydrogenchloride (**7**) and 25,27(4,4′-bis(ethoxybenzyl))-1,9-diaza-3,7-dithianonane-*p-tert*-butylcalix[4]arene dihydrogenchloride (**8**), respectively. Complexation studies of **7** and **8** with Zn(II), Cd(II) and Hg(II) ions were carried out by potentiometric titration. Compounds **7** and **8** selectively form 1 : 1 complexes with Hg(II), and their stability constants (log Ks) were estimated to be 4.47 ± 0.08 and 3.20 ± 0.13, respectively. From spiecies distribution plots, **7** and **8** were found to form the highest amount of 1 : 1 complexes with Hg(II) at pH 8.7 and 9.1, respectively.

Key words: azathiol, *p-tert*-butylcalix[4]arene, potentiometric titration, heavy metal ion complexing agents

1. Introduction

Heavy metals such as cadmium and mercury are toxic substances requiring to be removed from environments. One possible way is to extract these harmful metals from waters or soils by efficient extractants. Chemists thus play a major role in designing and preparing suitable ligands for this purpose. Important things to consider to obtain useful ligands are the complexation ability of a designed ligand towards heavy metal ions and the selectivity of the ligand for extracting a specific metal ion. This can be controlled by donor atoms and the topology of ligands. Roundhill and coworkers demonstrated elegant examples of using calix[4]arene de-

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rivatives containing sulfur donor atoms as extractants in heavy metal ion extraction [1–5].

Potentiometric titration is a useful technique to obtain information concerning stability of metal complexes and solution behaviors of metal ions and ligands [6]. Arnaud-Neu and coworkers demonstrated use of this technique in determining stability constants of metal complexes of *p-tert*-butylcalix[4]arene derivatives [7, 8]. Recently, we reported the synthesis of a calix[4]arene derivative containing a N, S and O donor set employing a metal template technique [9]. This compound was meant to be an extractant for heavy metal ions such as cadmium and mercury since it contains soft binding sites. We have extended our work by synthesizing heavy metal ion receptors containing *p-tert*-butylcalix[4]arene as building blocks employing condensation reactions. This article reports the synthesis and characterization of a series of closed ring *p-tert*-butylcalix[4]arene derivatives containing both N- and S-donor sets. Two derivatives possessing different cavity sizes are then transformed to their ammonium forms, 25,27(2,2′-bis(ethoxybenzyl))-1,9-diaza-3,7-dithianonane-*p-tert*-butylcalix[4]arene dihydrochloride (**7**) and 25,27(4,4′-bis(ethoxybenzyl))-1,9-diaza-3,7-dithianonane-*p-tert*-butylcalix[4]arene dihydrochloride (**8**). The stability constants of complexes between these ligands and heavy metal ions such as Cd(II) and Hg(II) were determined by potentiometric titration.

2. Experimental

2.1. MATERIALS

All materials and solvents were standard reagents and used without further purification unless otherwise noted. Commercial grade solvents such as acetone, dichloromethane and methanol were distilled and stored over 4 Å molecular sieve. Reagents were purchased from Merck, J. T. Baker or Fluka. $Zn(CF_3SO_3)_2$, $CdCl_2$ and $Hg(CF_3SO_3)_2$ were obtained from Aldrich, Merck and Strem, respectively, and were vacuum dried and kept in a dessicator before use. The compound 25,27(2,2′-bis(ethoxy)benzaldehyde))-*p-tert*-butylcalix[4]arene (**1**) was prepared according to the published procedure [10]. Preparation of the dithia diamine compounds, 1,8-diaza-3,6-dithiaoctane and 1,9-diaza-3,7-dithianonane, were prepared as described in the literature [11, 12].

2.2. ANALYTICAL PROCEDURES

The ^{1}H-NMR spectra were recorded at 200 MHz on a Bruker ACF200 NMR spectrometer. The IR spectra were obtained on a Nicolet Impact 410 FTIR spectrophotometer. Mass spectra were determined using a VG-Analytical ZAB HF mass spectrometer. Elemental analyses were carried out on a Perkin Elmer Elemental Analyser 2400 CHN at the Scientific and Technological Research Equipment Center of Chulalongkorn University.

2.3. SYNTHETIC PROCEDURES

2.3.1. *Preparation of 25,27(4,4′- bis(ethoxybenzaldehyde))-p-tert-butylcalix[4]arene (*2*)*

A 1-L 2-necked round bottom flask containing *p-tert*-butylcalix[4]arene (11.70 g, 18.1 mmol), K_2CO_3 (20.00 g, 145.6 mmol) and acetonitrile (350 mL) was added dropwise to a solution of 4-(2-bromoethoxy)benzaldehyde (9.53 g, 41.7 mmol) in acetonitrile (100 mL). The reaction mixture was heated at reflux under nitrogen for 53 h. After cooling to room temperature, K_2CO_3 was filtered off and washed with a large amount of acetone and dichloromethane. The filtrate was concentrated by rotary evaporation to yield a creamy caramel-like residue. The residue was dried on a rotary evaporator to yield a white solid mixture. The mixture was then chromatographed on a silica gel column with 2% acetone in dichloromethane as eluant. The compound **2** was obtained as white solid after solvent removal (9.16 g, 54%). ^{1}H NMR (200 MHz, CDCl$_3$) 9.90 (2H, s, C*H*O), 7.85 [4H, d, *J* (HH) 8.8 Hz, Ar*H$_A$H$_B$*], 7.23 [4H, d, *J* (HH) 8.8 Hz, Ar*H$_A$H$_B$*], 7.35 (2H, s, ArO*H*), 7.06 (4H, s, HOAr*H*), 6.87 (4H, s, ROAr*H*), 4.37 and 3.33 [8H, dd, *J* (HH) 13.1 Hz, ArC*H$_A$H$_B$*Ar], 4.33 (8H, s, OC*H$_2$*C*H$_2$*O), 1.29 (18H, s, HOAr-*t*-C$_4$*H$_9$*), 1.03 (18H, s, ROAr-*t*-C$_4$*H$_9$*). IR (KBr, $\nu_{C=O}$, cm^{-1}): 1695. FAB MS (m/z): 944.2. Anal. Calcd. for C$_{62}$H$_{72}$O$_8$: C, 78.77; H, 7.66. Found: C, 78.25; H, 8.05.

2.3.2. *Preparation of 25,27(2,2′- bis(ethoxybenzyl))-1,9-diimine-3,7-dithianonane-p-tert-butylcalix[4]arene (*3*)*

A mixture of **1** (2.03 g, 2.15 mmol), dichloromethane (20 mL) and ethanol (200 mL) was placed in a 500-mL 2-necked round bottom flask. After complete dissolution of **1**, an ethanolic solution (30 mL) of 1,9-diaza-3,7-dithianonane (0.49 g, 2.55 mmol) was added dropwise into the mixture. The reaction was heated at reflux under nitrogen atmosphere for 9 h to afford a white precipitate. After allowing the reaction mixture to cool to room temperature, the precipitate was then filtered and washed with methanol (2.02 g, 85%). ^{1}H NMR (200 MHz, CDCl$_3$) 8.82 (2H, s, C*H*=N), 7.94-6.91 (8H, m, Ar*H$_A$H$_B$H$_C$H$_D$*), 7.40 (2H, s, ArO*H*), 7.03 (4H, s, HOAr*H*), 6.84 (4H, s, ROAr*H*), 4.32 and 3.37 [8H, dd, *J* (HH) 12.9 Hz, ArC*H$_A$H$_B$*Ar], 4.38 (8H, s, OC*H$_2$*C*H$_2$*O), 3.54 (4H, t, NC*H$_2$*CH$_2$S), 2.59 (4H, t, NCH$_2$C*H$_2$*S), 2.48 (4H, t, SC*H$_2$*CH$_2$CH$_2$S), 1.69 (2H, q, SCH$_2$C*H$_2$*CH$_2$S), 1.30 (18H, s, HOAr-*t*-C$_4$*H$_9$*), 0.98 (18H, s, ROAr-*t*-C$_4$*H$_9$*). FAB (m/z): 1103.4. IR (KBr, $\nu_{C=N}$, cm^{-1}): 1634. Anal. Calcd. for C$_{69}$H$_{86}$O$_6$N$_2$S$_2$: C, 75.10; H, 7.85; N, 2.54. Found: C, 75.07; H, 7.86; N, 2.62.

2.3.3. *Preparation of 25,27(4,4′- bis(ethoxybenzyl))-1,9-diimine-3,7-dithianonane-p-tert-butylcalix[4]arene (*4*)*

In the same manner to the synthesis of **3**, a reaction between **2** (1.01 g, 1.07 mmol) and 1,9-diaza-3,7-dithianonane (0.24 g, 1.23 mmol) yielded **4** (0.84 g, 71%). ^{1}H

NMR (200 MHz, CDCl$_3$) 8.19 (2H, s, CH=N), 7.62 [4H, d, J (HH) 8.8 Hz, ArH_AH$_B$], 6.90 [4H, d, J (HH) 8.8 Hz, ArH_AH$_B$], 7.33 (2H, s, ArOH), 7.01 (4H, s, HOArH), 6.82 (4H, s, ROArH), 4.36 and 3.27 [8H, dd, J (HH) 12.8 Hz, ArCH_AH$_B$Ar], 4.29 (8H, s, OCH_2CH_2O), 3.75 (4H, t, NCH_2CH$_2$S), 2.81 (4H, t, NCH$_2$C H_2S), 2.64 (4H, t, SCH_2CH$_2$CH_2S), 1.87 (2H, q, SCH$_2$CH_2CH$_2$S), 1.25 (18H, s, HOAr-t-C$_4$H$_9$), 0.98 (18H, s, ROAr-t-C$_4$H$_9$). IR (KBr, $\nu_{C=N}$, cm^{-1}): 1642. Anal. Calcd. for C$_{69}$H$_{86}$O$_6$N$_2$S$_2$: C, 75.10; H, 7.85; N, 2.54. Found: C, 75.54; H, 7.82; N, 2.48.

2.3.4. *Preparation of 25,27(2,2′- bis(ethoxybenzyl))-1,8-diimine-3,6-dithianonane-p-tert-butylcalix[4]arene (5)*

Similarly, a reaction between **1** (1.03 g, 1.09 mmol) and 1,8-diaza-3,6-dithianonane (0.23 g, 1.28 mmol) yielded **5** (0.51 g, 43%). ^{1}H NMR (200 MHz, CDCl$_3$) 8.81 (2H, s, CH=N), 7.91-6.81 (8H, m, ArH_AH$_B$H$_C$H$_D$), 7.31 (2H, s, ArOH), 7.04 (4H, s, HOArH), 6.84 (4H, s, ROArH), 4.32 and 3.34 [8H, dd, J (HH) 13.3 Hz, ArCH_AH$_B$Ar], 4.38 (8H, s, OCH_2CH_2O), 3.51 (4H, t, NCH_2CH$_2$S), 2.57 (4H, t, NCH$_2$CH_2S), 2.50 (4H, s, SCH_2CH_2S), 1.26 (18H, s, HOAr-t- C$_4$H$_9$), 0.96 (18H, s, ROAr-t- C$_4$H$_9$). FAB (m/z): 1089.3. IR (KBr, $\nu_{C=N}$, cm^{-1}): 1643. Anal. Calcd. for C$_{68}$H$_{84}$O$_6$N$_2$S$_2$: C, 74.96; H, 7.77; N, 2.57. Found: C, 74.24; H, 7.96; N, 2.46.

2.3.5. *Preparation of 25,27(4,4′- bis(ethoxybenzyl))-1,8-diimine-3,6-dithianonane-p-tert-butylcalix[4]arene (6)*

Similarly, a reaction between **2** (0.97 g, 1.03 mmol) and 1,8-diaza-3,6-dithianonane (0.25 g, 1.39 mmol) yielded **5** (0.45 g, 40%). ^{1}H NMR (200 MHz, CDCl$_3$) 8.17 (2H, s, CH=N), 7.65 [4H, d, J (HH) 8.8 Hz, ArH_AH$_B$], 6.91 [4H, d, J (HH) 8.8 Hz, ArH_AH$_B$], 7.76 (2H, s, ArOH), 7.03 (4H, s, HOArH), 6.90 (4H, s, ROArH), 4.35 and 3.30 [8H, dd, J (HH) 13.0 Hz, ArCH_AH$_B$Ar], 4.26 (8H, s, OCH_2CH_2O), 3.77 (4H, t, NCH_2CH$_2$S), 2.80 (4H, t, NCH$_2$CH_2S), 2.78 (4H, t, SCH_2CH_2S), 1.25 (18H, s, HOAr-t-C$_4$H$_9$), 1.05 (18H, s, ROAr-t-C$_4$H$_9$). IR (KBr, $\nu_{C=N}$, cm^{-1}): 1640. Anal. Calcd. for C$_{68}$H$_{84}$O$_6$N$_2$S$_2$: C, 74.96; H, 7.77; N, 2.57. Found: C, 73.33; H, 7.46; N, 2.22.

2.3.6. *Preparation of 25,27(2,2′-bis(ethoxybenzyl))-1,9-diaza-3,7-dithianonane-p-tert-butylcalix[4]arene dihydrochloride (7)*

Into a solution of **3** (0.94 g, 0.86 mmol) in dichloromethane (100 mL) was added NaBH$_4$ (0.67 g, 17.67 mmol). The mixture was stirred under nitrogen atmosphere for 24 h at room temperature. Water was then added to quench excess NaBH$_4$. The organic layer was subsequently separated from the aqueous layer, and was extracted with several portions of water until the pH of the aqueous phase reached 7. The combined organic layers were later dried over sodium sulfate, filtered and evaporated to dryness to obtain a white solid. A solution of HCl/CH$_3$OH (0.74% V/V) was slowly added to dissolve the white solid, and the addition was continued until

the pH of the solution reached 1. Upon slow evaporation of methanol, the product precipitated as white solid (0.65 g, 65%). ^{1}H NMR (200 MHz, CDCl$_3$) 9.71 (4H, broad, ArCH$_2$NH_2^+), 7.78 (2H, s, ArOH), 7.38-6.88 (8H, m, Ar$H_A H_B H_C H_D$), 6.94 (4H, s, HOArH), 6.85 (4H, s, ROArH), 4.97 and 4.43 (12H, broad, OCH_2CH_2O and ArCH_2N$^+$), 4.29 and 3.19 [8H, dd, J (HH) 12.9 Hz, ArC$H_A H_B$Ar], 3.14 (8H, broad, NCH_2CH$_2$S and NCH$_2$CH_2S), 2.60 (4H, broad, SCH_2CH$_2$CH_2S), 1.99 (2H, broad, SCH$_2$CH_2CH$_2$S), 1.20 (18H, s, HOAr-t-C$_4H_9$), 0.99 (18H, s, ROAr-t-C$_4H_9$). Anal. Calcd. For C$_{69}$H$_{92}$O$_6$N$_2$S$_2$Cl$_2$: C, 70.20; H, 7.86; N, 2.37. Found: C, 70.18; H, 7.70; N, 2.30.

2.3.7. *Preparation of 25,27(4,4′- bis(ethoxybenzyl))-1,9-diaza-3,7-dithianonane-p-tert-butylcalix[4]arene dihydrochloride (8)*

In the same fashion to the preparation of **7**, reduction and protonation of **4** (1.00 g, 0.91 mmol) with NaBH$_4$ (0.70 g, 18.40 mmol) and HCl/CH$_3$OH, respectively, gave a white solid of **8** (0.64 g, 55%). ^{1}H NMR (200 MHz, CDCl$_3$) 9.35 (4H, broad, Ar CH$_2$NH_2^+), 7.66 [4H, d, J (HH) 8.6 Hz, Ar$H_A H_B$], 7.08 [4H, d, J (HH) 8.6 Hz, Ar$H_A H_B$], 7.96 (2H, s, ArOH), 7.02 (4H, s, HOArH), 6.91 (4H, s, ROArH), 4.37 and 3.32 [8H, dd, J (HH) 12.9 Hz, ArC$H_A H_B$Ar], 4.65 and 4.39 (12H, broad, OCH_2CH_2O and ArCH_2NH_2^+), 3.92 (4H, broad, N CH_2CH$_2$S), 2.96 (4H, broad, NCH$_2$CH_2S), 2.46 (4H, broad, SCH_2CH$_2$CH_2S), 1.89 (2H, broad, SCH$_2$CH_2CH$_2$S), 1.22 (18H, s, HOAr-t-C$_4H_9$), 1.06 (18H, s, ROAr-t-C$_4H_9$). Anal. Calcd. For C$_{69}$H$_{92}$O$_6$N$_2$S$_2$Cl$_2$: 70.20; H, 7.86; N, 2.37. Found: C, 70.38; H, 7.47; N, 2.31.

2.4. STABILITY CONSTANT DETERMINATION

The inert background electrolyte used in titrations was Bu$_4$NCF$_3$SO$_3$ prepared in a mixture of 10% CH$_2$Cl$_2$ in CH$_3$OH (0.05 M). Stock solutions of Zn(II) and Cd(II) (0.01 M) and Hg(II) (0.005 M) were prepared by dissolution of weighed quantities of dried metal salts in the inert background solution. Solutions of the ligands **7** and **8** (0.001 M) and the titrant base, Bu$_4$NOH, (0.05 M) were also prepared in the inert background solution. Standard solutions of HCl (0.01 M) and HClO$_4$ (0.01 M) in the inert background solution were used to adjust the pH during electrode calibrations [7] and titration experiments.

The stability constants of the complexes were obtained potentiometrically using a competitive method with proton. The concentrations of [H$^+$] were measured by a combined glass electrode (Mettler DG113-SC) connected to an automatic ti-trator (Mettler DL25). All titration experiments were performed at 25 °C. For com-plexation constant determination, typically a 10 mL portion of a stock solution of a ligand was added to a metal solution under argon atmosphere and subsequently titrated with Bu$_4$NOH. For each determination at least four experiments were performed with different mole ratios of metal:ligand. The stability constants were calculated using the program "SUPERQUAD" [13]. The protonation constants of

the free ligands, determined from titrations of ligands in the absence of metal, and metal hydroxide species, MOH^+, were included in the refinement procedures. The stability constant of the mercury hydroxide species, $HgOH^+$, was $\log K = -9.55$.

3. Results and Discussion

3.1. PREPARATION AND CHARACTERIZATION OF THE LIGANDS

Our group has modified *p-tert*-butylcalix[4]arene at the lower rim phenoxide moieties by attaching two ethoxybenzaldehyde groups via nucleophilic substitution reactions of *p-tert*-butylcalix[4]arene and 2-(2′-bromoethoxy)benzaldehyde or 4-(2-bromoethoxy)benzaldehyde in the presence of K_2CO_3. The resulting dialdehyde *p-tert*-butylcalix[4]arenes, **1** and **2** are suitable for building macrocyclic or chelating frameworks for metal ion binding. Dropwise additions of ethanolic solutions of 1,9-diaza-3,7-dithianonane or 1,8-diaza-3,6-dithiaoctane into solutions (10% dichloromethane in ethanol) of compounds **1** or **2** (1 : 1 stoichiometry) yielded a variety of Schiff base compounds. These reactions require high dilution conditions to prevent the formation of the polymeric products that may occur [14]. The ligands **3**, **4**, **5** and **6** precipitated out of the reaction mixtures in 85, 71, 43 and 40% yields, respectively. The yields of compounds **3** and **4** containing a propylene linkage between two N-atoms are about twice as high as those of compounds **5** and **6** which contain an ethylene linkage. The ortho-substituted diaza dithiol compounds, **3** and **4**, can be obtained in higher yields than the para-substituted derivatives, **5** and **6**. This may be attributed to polymerization which may simultaneously occur with condensation reactions. The more steric ortho-substituted aldehyde, **1**, should be less susceptible to polymerisation than the less steric para-substituted **2**. Due to the low yields of compounds **5** and **6**, they were not used for further studies. Only compounds **3** and **4** were, therefore, used. Reduction of **3** and **4** was carried out by $NaBH_4$, and the reduced products were then protonated by a solution of HCl in methanol (0.74% v/v) in order to produce more stable ammonium chloride derivatives, **7** and **8**, respectively. In addition, these two compounds are also suitable for further potentiometric studies. The preparation for compounds **3–8** are depicted in Scheme 1.

Compounds **3–8** were characterized by ^{1}H NMR spectroscopy, FAB MS, FTIR and elemental analysis. ^{1}H NMR spectra of the Schiff base compounds **3**, **4**, **5** and **6** show singlet signals due to imine protons at 8.82, 8.19, 8.81 and 8.17 ppm, respectively. Furthermore, IR spectra of compounds **3**, **4**, **5** and **6** show bands due to C=N stretching at 1634, 1642, 1643 and 1640 cm^{-1}, respectively. FAB mass spectra of compounds **3** and **5** show strong peaks at m/z 1103.4 and 1089.3, respectively, which agrees with the molecular weight of the proposed structures. Upon reduction and protonation of **3** and **4** to **7** and **8**, signals of the imine protons disappeared from the ^{1}H NMR spectra of **7** and **8**, and the broad signals due to the RN^+H_2 protons appeared instead at 9.71 and 9.35 ppm, respectively. The significant downfield shift is strong evidence for the positive charges at nitrogen atoms. In addition, [1]H
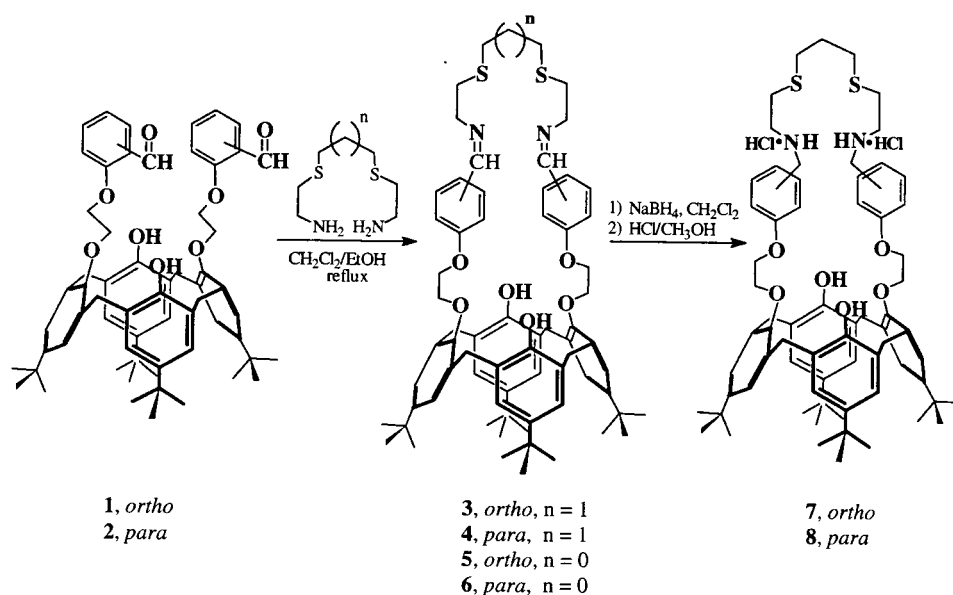
Scheme 1.

NMR spectra of compounds **3–8** suggest that calix[4]arene compartments are in a cone conformation judging by the appearance of a pair of doublet signals due to methylene bridge protons with a coupling constant of around 13 Hz. All elemental analysis results agree well with the proposed structures of compounds **3–8**.

3.2. COMPLEXATION STUDIES

In order to investigate the complexation ability of the diaza dithia derivatives, compounds **7** and **8** were used in potentiometric titration experiments. Protonation constants and complex stability constants were calculated by the program SUPERQUAD. Each of compounds **7** and **8** was estimated to have two protonation constants [15]: $\log K_1 = 8.67 \pm 0.01$, $\log K_2 = 7.82 \pm 0.03$ and $\log K_1 = 8.47 \pm 0.02$, $\log K_2 = 7.87 \pm 0.04$ for **7** and **8**, respectively. The protonation constants indicate that the basicity or donor ability of these two ligands is comparable. Stability constants of metal complexes of ligands **7** and **8** were also calculated by SUPERQUAD and shown in Table I. The results show that ligands **7** and **8** do not form 1 : 1 complexes (ML^{2+}) with Zn(II) and Cd(II) ions at all. However, both **7** and **8** form hydroxide complexes with Zn(II) and Cd(II), i.e., $ZnL(OH)_2$ and $CdL(OH)_2$, respectively, with low complex stability constants. Considering the most preferable geometry of Zn and Cd complexes, tetrahedral geometry, we think that our ligand environments are unsuitable for forming complexes with these ions. The ethylene and propylene pendant arms of both ligands may be too strained to rearrange themselves to support a tetrahedral geometry. The

Table I. Stability constants of complexes of ligands **7** and **8** with Zn(II), Cd(II) and Hg(II)

Complexes	log K		
	M = Zn(II)	M = Cd(II)	M = Hg(II)
M[**7**]$^{2+}$	–	–	4.47 ± 0.08
M[**7**](OH)$_2^{\mathrm{a}}$	-14.82 ± 0.09	-17.1 ± 0.1	–
M[**8**]$^{2+}$	–	–	3.2 ± 0.1
M[**8**](OH)$_2^{\mathrm{a}}$	-15.54 ± 0.06	-16.80 ± 0.07	–

$^{\mathrm{a}}$ Obtained from the following equilibrium: $M^{2+} + L + 2OH^- \rightleftharpoons$ $ML(OH)_2$: L = [**7**] or [**8**], M = Zn or Cd.

The log K values were calculated from the computer refinement.

N_2S_2 donor sets of **7** and **8** coordinate to metal ions in square planar fashions. A ligand, *N,N'*-bismercaptoethyl-1,5-diazacyclooctane (bme-daco) [16], prepared by Darensbourg and coworkers has a similar donor set to ligands **7** and **8**, and was found to react with $Zn(acac)_2$ to give a dinuclear square pyramidal complex, [Zn(bme-daco)]$_2$ [17], rather than a mononuclear tetrahedral complex due to ligand constraint. Nevertheless, ligands **7** and **8** can accommodate an octahedral geometry since a metal may use the N_2S_2 donor sets of **7** and **8** as equatorial ligands and two OH^- ions as axial ligands.

The ligands **7** and **8** form 1 : 1 complexes towards Hg(II) with stability constant values of 4.47 and 3.20, respectively. Hosseini et al. have found that *p-tert*-butyltetramercaptocalix[4]arene can form a complex with Hg(II) by linear S-coordinations [18]. However, in the case of **7** and **8**, we are not so certain that the geometry of the complexes would be linear since compound **8** which has a bigger cavity of the receptor unit forms a less stable complex with Hg(II). The structures of Hg[**7**]$^{2+}$ and Hg[**8**]$^{2+}$ must be elucidated by X-ray crystallography in the future.

Besides stability constants, potentiometric titration can give more information on the behavior of metals and ligands in solution. Species distribution plots of the ligands **7** and **8** towards Hg(II) are illustrated in Figure 1. The highest amount of 1 : 1 complexes with **7** and **8** occurred at pH 8.7 (74%) and 9.1 (35%), respectively. These data may be used as a direction for the extraction of Hg(II) by ligands **7** and **8**. It should be noted that **7** is a better ligand for complexing Hg(II). This suggests that the cavity size of a N_2S_2 donor set in **7** may be more suitable for binding Hg(II) than that in **8**.

4. Conclusion

We have synthesized a variety of *p-tert*-butylcalix[4]arene derivatives containing N_2S_2 donor sets and demonstrated use of certain derivatives, compounds **7** and **8**, to form complexes with heavy metal ions in group IIB. Both ligands were found to selectively form complexes with Hg(II) ion but not Cd(II) and Zn(II). Ligand **7**
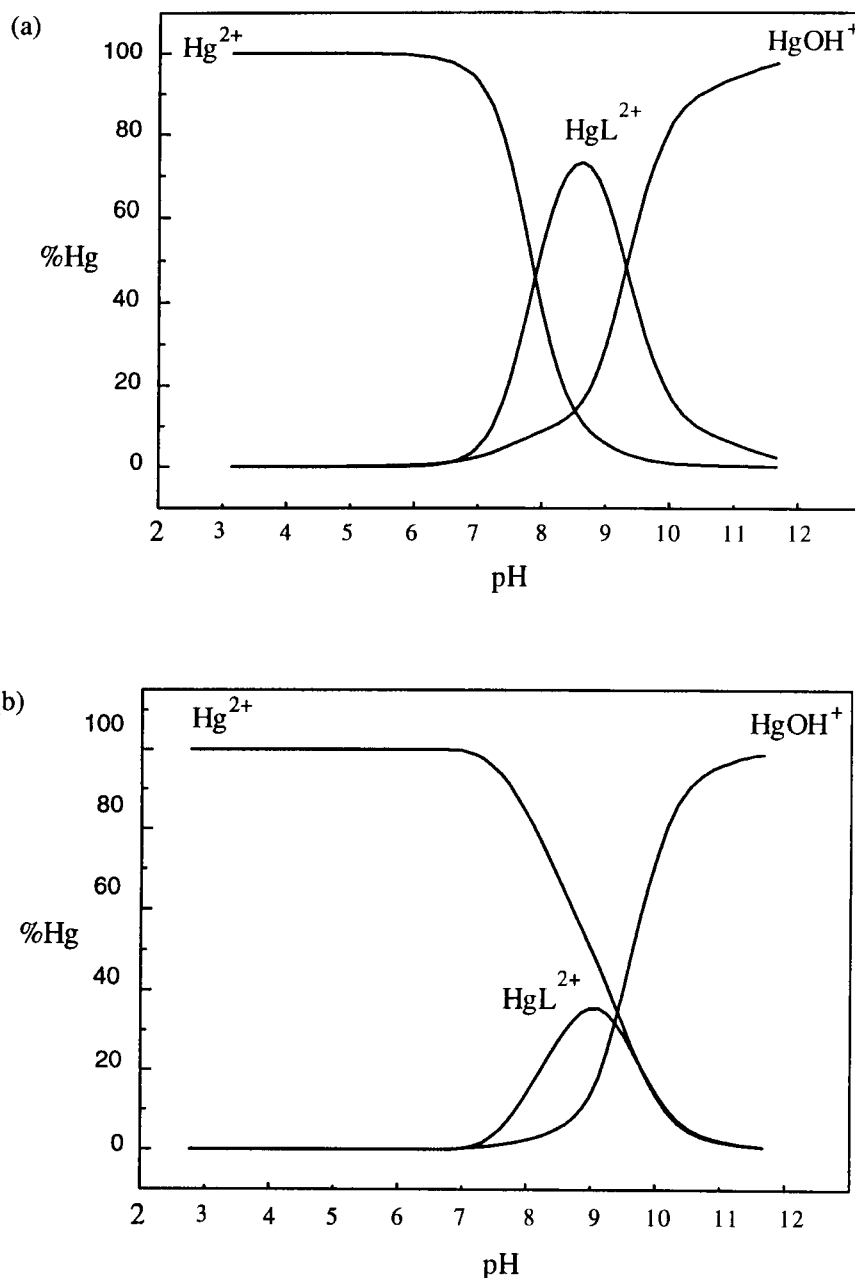
Figure 1. Species distribution plots: (a) L = **7** and (b) L = **8**.

shows better properties for metal complexation than **8** does. The best conditions for ligands **7** and **8** to form complexes with Hg(II) are at pH 8.7 and 9.1, respectively.

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